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Electron Transfer Reactions of Tris(toluene-3,4-dithiolato)molybdenum(VI) with Organic Compounds

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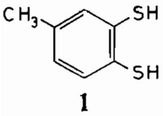
Abstract

The compound $[Mo(tdt)_3]$ (tdt = toluene-3,4-dithiolate) reacts with aromatic hydrocarbons, *N*-heterocycles, riboflavin and molybdoenzyme substrates such as purines and aldehydes forming the reduced species $[Mo(tdt)_3]^-$ and organic radicals. The reactions were followed with UV–Vis and ESR spectroscopy; organic radicals were trapped with 2-methyl-2-nitrosopropane and 5,5-dimethyl-1-pyrroline-*N*-oxide. The stoichiometry of the reaction with naphthalene and triphenylphosphine, determined by Job's method of continuous variations, was 1:1.

The solvent was dichloromethane. For the reactions to occur the presence of a base was necessary, a reactant or added ethanol for the hydrocarbon reactions. The reactions involved electron transfer from the organic molecule to the molybdenum dithiolate.

Introduction

Tris-dithiolato complexes of transition metals have been much studied on account of their trigonal prismatic structures and electron transfer reactions which involve orbitals of mainly ligand character [1–7]. Complexes $M(tdt)_3$ (M = Mo, Re, Tc; H_2tdt = toluene-3,4-dithiol) (**1**) exhibit a so-called solvent effect; the colours of solutions depend on the donor properties and polarities of the solvents [7, 8]. In this paper we describe reactions of the molybdenum complex $[Mo(tdt)_3]$ [2] with anthracene, naphthalene, triphenylphosphine, pyridazine, acetaldehyde, salicylaldehyde, xanthine, 1-serine, riboflavin, and cysteine. Reactions were followed by UV–Vis and ESR spectroscopy. Our object was to determine the nature of the products and the reaction stoichiometry.



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Experimental

Preparation of Tris(toluene-3,4-dithiolato)molybdenum(VI)

The complex was synthesised according to the modified method of Mitchell and Butcher [13]. To a warm solution of ammonium heptamolybdate (2.19 g, 2×10^{-3} mol) in H_2SO_4 3 M (*ca.* 60 cm^3) saturated with nitrogen was added H_2tdt (5 cm^3, 2×10^{-3} mol) in 2 M NaOH (*ca.* 33 cm^3) and diluted to 60 cm^3 with water and saturated with nitrogen. The addition of the ligand was dropwise and the temperature was kept at between 60–65 °C. The dark green product was filtered in air and dried over P_2O_5. The solid was purified by column chromatography using silica gel 60–120 and eluted with a mixture of cyclohexane–dichloromethane 3:1. *Anal.* Calc. for $C_{21}H_{18}MoS_6$: C, 45.2; H, 3.24; Mo, 17.2. Found: C, 45.0; H, 3.53; Mo. 17.5%. UV–Vis, dichloromethane $[\lambda_{max}$ (nm) $(10^{-3}\ \epsilon_{max}/m^2\ mol^{-1})]$ 434(18.5), 684(22.3).

Physical Measurements

Electronic spectra were recorded on Unicam SP 1800 and Perkin–Elmer Lambda 3 spectrophotometers. Electron spin resonance spectra were recorded on a Varian E3 spectrometer calibrated with diphenylpicrylhydrazide (g = 2.0023).

Procedure

All operations were carried out under nitrogen or *in vacuo*. Solvents were dried and distilled before use. Solutions of $[Mo(tdt)_3]$ and reactants (*ca.* 10^{-2} mol l^{-1}) in CH_2Cl_2 and ethanol were used. Generally the reactants were added to the $[Mo(tdt)_3]$ solution.

Reactions were followed by UV–Vis and ESR spectroscopy. Times taken to reach equilibrium varied from a few hours to days. In some experiments

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free radicals were trapped with the spin-trapping agents 5,5-dimethyl-1-pyrroline-*N*-oxide and 2-methyl-2-nitrosopropane.

Results and Discussion

Reactions of tris(toluene-3,4-dithiolato)molybdenum(VI), $[Mo(tdt)_3]$, with aromatic hydrocarbons, nitrogen heterocyclics, purines and aldehydes have been studied by UV–Vis and ESR spectroscopy. Our general conclusion is that the reactions proceed in two stages via eletron transfer from the organic reactants. The stoichiometry of the first stage is 1:1; the products are the paramagnetic $[Mo(tdt)_3]^-$ and an organic radical. In the second stage $[Mo(tdt)_3]^-$ is reduced to $[Mo(tdt)_3]^{2-}$.

UV–Vis Spectra

UV–Vis spectroscopy was used to identify the species in the reaction mixtures and to determine the reaction stoichiometry. Typical spectra of 1:1 mixtures at equilibrium are shown in Fig. 1. We see the peaks of $[Mo(tdt)_3]^-$ [13, 18]. When the reducing agent was in excess these peaks disappeared and a band at *ca.* 600 nm remained. This peak is characteristic of the two-electron reduced species, $[Mo(tdt)_3]^{2-}$ [13, 18].

The stoichiometry of the first stage of the reaction with triphenylphosphine and naphthalene, which both react fast, was determined by Job's method of continuous variations. A typical Job's plot is shown in Fig. 2. The maximum absorbance is at a mole fraction 0.5. The stoichiometry is clearly 1:1. Results with naphthalene were similar.

Electron Spin Resonance Spectra

The ESR spectra of $[MoOCl_5]^{2-}$ in concentrated hydrochloric acid, $[Mo(tdt)_3]$ in diglyme reduced with sodium borohydride, and the reaction mixture of $[Mo(tdt)_3]$ and naphthalene are shown in Fig. 3. The Mo(V) spectra show typically a strong central line and six hyperfine lines due to the magnetic ($I = 5/2$) isotopes ^{95}Mo and ^{97}Mo which have 25% abundance in natural Mo. The *g*-values, taken at the turning points of the derivative curves, are included in Fig. 3 and agree well with literature values.

The spectrum of $[Mo(dtd)_3]$ with naphthalene, see Fig. 3c, is typical of the spectra of mixtures of $[Mo(tdt)_3]$ with naphthalene, anthracene, triphenylphosphine, tetramethylethylenediamine, acetaldehyde, salicylaldehyde, serine, cysteine, pyridazine, xanthine and riboflavin. Spectra representative of the various compound types are shown in Fig. 4. The strong central line in the spectra of the reaction mixtures is more intense relative to the hyperfine intensity than for the $[Mo(V)(tdt)_3]^-$ species formed by reduction of $[Mo(tdt)_3]$ with $NaBH_4$. This is clear from Fig. 3b. With a spectrometer gain set to record the hyperfine intensity the intensity of the central line is too high for it to be recorded. Conversely, if we record the central line the hyperfine can hardly be distinguished from background. We conclude that in the reaction mixtures there is a new species resonating near $g = 2.002$, evidently a free radical. The central line became split when the field axis was expanded, showing two species. To confirm the formation of a free radical we reacted

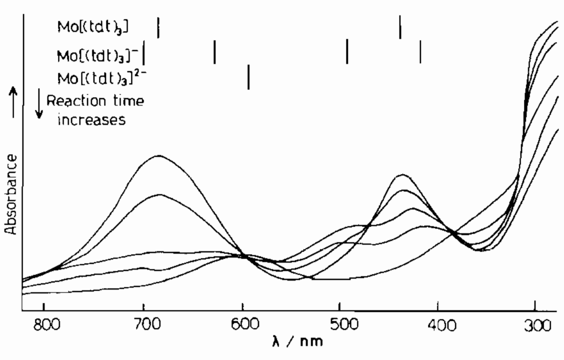

Fig. 1. Reaction of $[Mo(tdt)_3]$ (3.5×10^{-5} mol dm^{-3}) with naphthalene (7.0×10^{-5} mol dm^{-3}) in $EtOH/CH_2Cl_2$ showing change of UV–Vis spectrum with time during 1d.

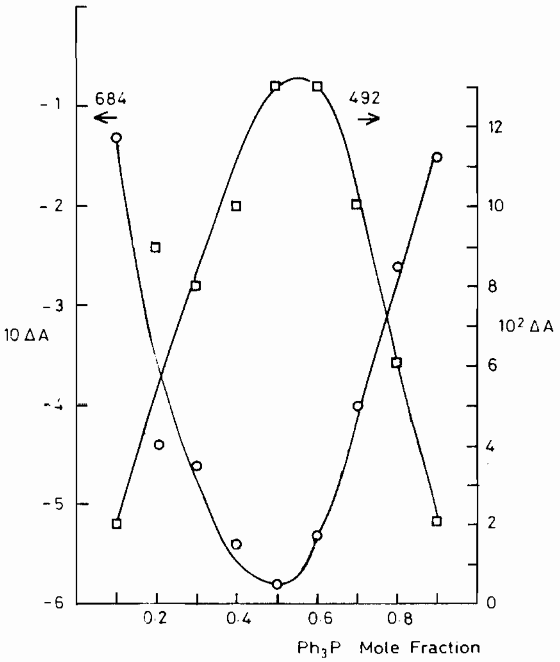

Fig. 2. Job's plot for the reaction between $[Mo(tdt)_3]$ and Ph_3P in CH_2Cl_2: difference (ΔA) between measured light absorbance at 684 and 492 nm and calculated light absorbance assuming no reaction plotted *vs.* mole fraction of Ph_3P. Total molar concentration was constant at 1.4×10^{-4} mol dm^{-3}. The 684 nm curve shows the disappearance of $[Mo(tdt)_3]$ and the 492 nm curve the formation of $[Mo(tdt)_3]^-$.

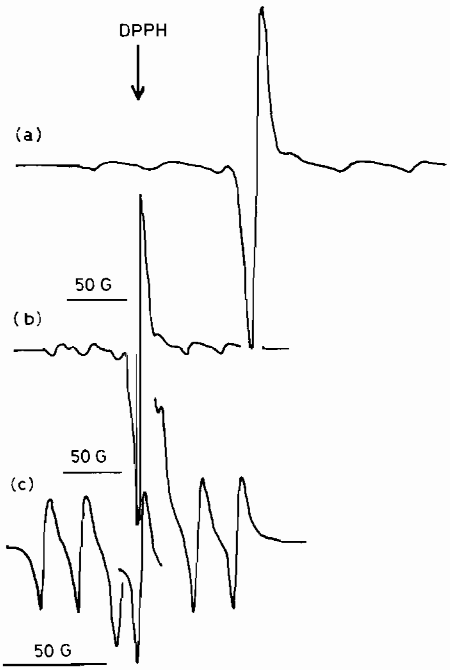

Fig. 3. Electron spin resonance spectra of: (a) Mo(V) in concentrated HCl ($\langle g \rangle$ 1.948, $\langle A \rangle$ 50 G); (b) [Mo(tdt)$_3$] in diglyme, reduced with NaBH$_4$ ($\langle g \rangle$ 2.002, $\langle A \rangle$ 29 G); [Mo(tdt)$_3$] and naphthalene in EtOH/CH$_2$Cl$_2$ ($\langle g \rangle$ 2.002, $\langle A \rangle$ 29 G). The vertical arrow is the diphenylpicrylhydrazyl (DPPH) calibrant, $g = 2.0023$.

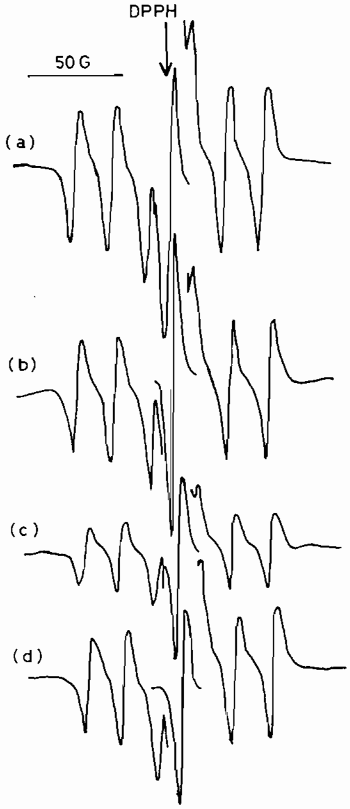

Fig. 4. Electron spin resonance spectra of mixtures of [Mo(tdt)$_3$] in CH$_2$Cl$_2$ and ethanol with: (a) salicyladehyde, (b) cysteine, (c) xanthine, (d) riboflavine. ESR parameters for Mo(V) same as Fig. 3b.

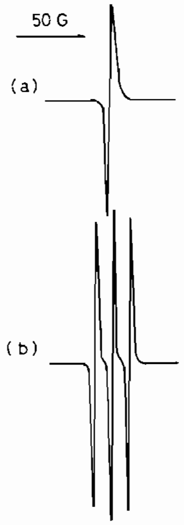

Fig. 5. ESR spectra of: (a) chloranil semiquinone free radical ($g = 2.0038$), and (b) after adding 2-methyl-2-nitrosopropane ($\langle g \rangle$ 2.0050, $\langle A \rangle$ 16 G).

[Mo(tdt)$_3$] with *N,N,N′,N′*-tetramethylethylenediamine (TMED), a compound which gives a particularly stable radical and hence a high radical concentration and an intense ESR signal. TMED reacted with [Mo(tdt)$_3$] in the same way as the other organic compounds and gave an intense central line. The reaction is evidently similar to that of the analogous compound *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine which forms a stable cation radical in reactions with the dithiolate complexes of molybdenum, tungsten, rhenium, and technetium [15, 16]. A spin-trapping technique was used to identifiy the free radicals.

Spin-trapping Experiments

Organic radicals formed in the electron-transfer reactions of organic molecules with [Mo(tdt)$_3$] were trapped by adding to the reaction mixture the spin-trapping agents 2-methyl-2-nitrosopropane and 5,5-dimethyl-2-pyrroline-*N*-oxide. We report the results with *N,N,N′,N*-tetramethylethylenediamine (TMED) as the donor molecule.

The type of spectrum to be expected when the trapping agent 2-methyl-2-nitrosopropane reacts with a free radical is shown in Fig. 5. The radicals were generated by the reaction of TMED with tetrachloro-1,4-benzoquinone (chloranil) in dichloromethane [17]. The ESR spectrum at our resolution was a

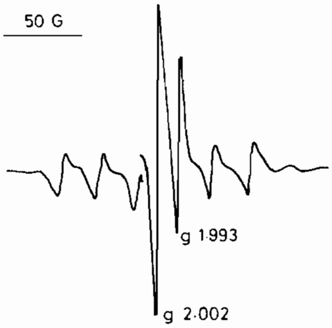

Fig. 6. ESR spectrum of the reaction mixture of $[Mo(tdt)_3]$ and tetramethylethylenediamine in CH_2Cl_2.

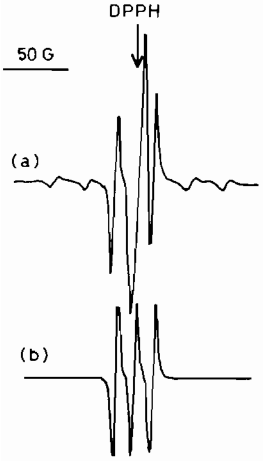

Fig. 7. ESR spectrum of the reaction of $[Mo(tdt)_3]$ and tetramethylethylenediamine in CH_2Cl_2 with the spin-trapping agent 2-methyl-2-nitrosopropane added: (a) after *ca.* 1 h, (b) after *ca.* 15 h.

single intense line. When the trapping agent 2-methyl-2-nitrosopropane was added this line split into a triplet in the magnetic field of the nitrogen nucleus ($I = 1$) of the trapping agent, see Fig. 5b.

Reaction of $[Mo(tdt)_3]$ with TMED in dichloromethane gave the ESR spectrum shown in Fig. 6. There were two strong central lines which we assign to the TMED radical and $[Mo(tdt)_3]^-$. In the presence of the trapping agent 2-methyl-2-nitrosopropane the spectrum shown in Fig. 7a was observed. There is a strong central triplet assigned to the free radical and weaker lines assigned to $[Mo(tdt)_3]^-$. The triplet is due to the interaction of the trapping agent with the TMED radical. When the solution was left overnight the resulting spectrum, Fig. 7b, showed only the central triplet. Clearly the molybdenum signal had disappeared owing to the formation of the diamagnetic $[Mo(tdt)_3]^{2-}$ species. These observations are evidence for the formation of $[Mo(tdt)_3]^-$ and an organic radical in the first stage of the reaction and the subsequent reduction of $[Mo(tdt)_3]^-$ to $[Mo(tdt)_3]^{2-}$.

Conclusions

The compound $[Mo(tdt)_3]$ undergoes electron transfer reactions with polynuclear hydrocarbons such as naphthalene and anthracene, with amines, N-heterocycles, purines including xanthine, with riboflavin and aldehydes forming the one-electron reduced species $[Mo(tdt)_3]^-$ and an organic radical. For the particular cases of naphthalene and triphenylphosphine a 1:1 reaction stoichiometry was demonstrated.

The presence of a base (which might be a reactant or ethanol in a mixed solvent) was necessary for reaction to occur. Presumably the redox reaction is promoted by ion-pair formation between the $[Mo(tdt)_3]^-$ anion and a cation radical (eqn. (1)) or the protonated base (B, eqn. (2)):

$$RH + [Mo(tdt)_3] \longrightarrow RH^{+\cdot} + [Mo(tdt)_3]^- \qquad (1)$$

$$RH + [Mo(tdt)_3] + B \longrightarrow R\cdot + [BH]^+ + [Mo(tdt)_3]^- \qquad (2)$$

In a slower reaction the two-electron reduced species $[Mo(tdt)_3]^{2-}$ is formed.

Formation of free radicals in redox reactions of organic electron-donor molecules with Mo(VI) species is well documented. For example, polynuclear hydrocarbons are converted to cation radicals in surface reactions with MoO_3 supported on alumina and silica and Mo(VI) is reduced to Mo(V) [19]. Similarly, flavosemiquone radicals are formed in reactions of Mo(VI) species in solution with riboflavin [20–24]. Recently we reported the formation of porphyrin cation radicals in surface reactions of porphyrins with oxomolybdenum(VI) species in hydroprocessing catalysts [25]. In the present work we have shown that $[Mo(tdt)_3]$ will also act as an electron acceptor in electron-transfer reactions with organic molecules. It is particularly interesting that the reactants include molybdoenzyme substrates such as xanthine and aldehydes.

Acknowledgement

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